

In Fig. 2 the values of  $\bar{\nu}_{P-S}$  calculated by use of eq. 3 are plotted against the experimentally observed values. It will be noted that the largest deviations are observed for the cyclohexyl compound, 11; the phenyl-bearing compounds, 16, 18, 6; and the trichloro derivative.

These results clearly indicate that the electronegativity of the substituents on the phosphorus atom plays a most important role in determining the frequency of the fundamental P=S vibration. The steric factors appear to be of secondary importance. The very strong association among molecules containing ethyl and methyl substituents undoubtedly accounts for the unusually low frequencies observed for the P=S vibrations in these molecules.

The range of 770–750  $\text{cm}^{-1}$  suggested by Thomas<sup>18</sup> for the frequency range of the P=S vibration in phosphine sulfides is obviously too narrow. The range for the P=Se vibration as reported by Thomas and Chittenden<sup>8</sup> is essentially correct but the limit at which

(18) Reference 6, p. 322.

this frequency may be observed needs to be lowered to at least 422  $\text{cm}^{-1}$ .

The use of a single force constant for the P=S link,<sup>1</sup> while it may provide a simplifying assumption made for the purpose of observing mass effects, must be considered a useful approximation. The wide range over which  $\bar{\nu}_{P-S}$  is observed (535–860  $\text{cm}^{-1}$ ) in addition to the obvious influence of the electronegativity of the phosphorus substituents means that  $k_{P-S}$  also must vary.

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## Magnetic Oxides of Molybdenum(V) and Tungsten(V) with the Ordered Perovskite Structure<sup>1</sup>

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Compounds with the type formula  $A_2B'B''O_6$  have been prepared in which A is an alkaline earth ion and B' is pentavalent molybdenum or tungsten. When B' is Fe(III), or Cr(III), ferrimagnetic compounds are obtained. The compounds are of the perovskite type and, in the case of the iron compounds, are shown by X-ray diffraction data to be ordered. Very weak superlattice lines were observed in the pattern of  $\text{Sr}_2\text{CrWO}_6$  but none was found in that of  $\text{Sr}_2\text{CrMoO}_6$ . Partial ordering for these compounds is suggested on the basis of their magnetic properties.  $\text{Ba}_3\text{Cr}_2\text{MoO}_9$  and  $\text{Ba}_3\text{Cr}_2\text{WO}_9$  have the hexagonal barium titanate structure and are not ferrimagnetic.

Compounds of the type  $A_2B'B''O_6$  tend to adopt the perovskite structure when A is a large cation capable of 12-fold coordination with oxygen while B' and B'' are smaller cations suitable for octahedral coordination. If the difference in charge of the B' and B'' cations is large, these ions assume an ordered arrangement in the perovskite lattice. This has been demonstrated with compounds such as  $\text{Ba}_2\text{ZnWO}_6$ ,<sup>2</sup>  $\text{Ba}_2\text{NaReO}_6$ ,<sup>3</sup> and  $\text{Ba}_2\text{FeReO}_6$ .<sup>4</sup>

In the ideal cubic perovskite structure the oxygen octahedra surrounding the B cations are regular, and each oxygen is shared by two B cations with a B–O–B angle of 180°. Such an arrangement is ideal for interaction of the B cations by the mechanism of super-

exchange.<sup>5</sup> With paramagnetic B cations of different moment in alternating B positions, the compound should exhibit ferrimagnetism. This was demonstrated in the case of rhenium(VI) compounds.<sup>4,6</sup> There was some doubt that this principle could be extended to the preparation of magnetic oxides of molybdenum(V) and tungsten(V) of the type  $A_2B^{III}B''O_6$ . A comparable compound,  $\text{Ba}_2\text{FeTaO}_6$ , showed no evidence of superstructure in its X-ray powder diffraction diagram.<sup>7</sup> On the other hand, differences in ionic radii of the two B cations has been shown to lead to an ordered arrangement in compounds such as  $\text{Ba}_2B^{III}\text{TaO}_6$  when B<sup>III</sup> is a rare earth ion.<sup>8</sup>

This paper describes the preparation and properties of the series of compounds  $A_2B^{III}B^VO_6$ , where B<sup>III</sup> is Fe or Cr and B<sup>V</sup> is Mo(V) or W(V).

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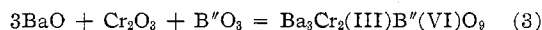
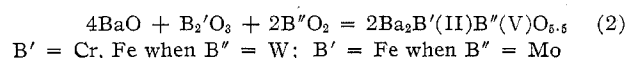
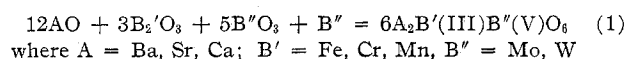
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## Experimental

The reactants used for the preparations were reagent grade chemicals in most instances. Barium oxide was made by the thermal decomposition of the peroxide at 950° for 24 hr. *in vacuo*. Strontium oxide was prepared by heating strontium carbonate in hydrogen at 1000° for 48 hr. The molybdenum and tungsten powders were commercial products of unknown purity.

Since the compounds to be prepared were intended to contain pentavalent molybdenum and tungsten, all preparations were carried out by heating the pellets of reagent mixtures in evacuated silica capsules at 900–1000°. Ordinarily the product was removed after a short period of heating, ground in an agate mortar, repelleted, and heated again *in vacuo* for 24 hr. With some preparations this procedure was repeated several times. The compositions of the mixtures and the expected products are indicated in eq. 1 to 3.



The products were examined microscopically and by X-ray powder diffraction. They were black microcrystalline powders usually contaminated with alkaline earth molybdates or tungstates. The formation of these impurities could be avoided by preparing the oxygen-deficient phase as indicated in eq. 2. The properties of the oxygen-deficient products have not yet been examined. Several of the desired compounds were strongly attracted to a magnet. This provided a means of separation from the diamagnetic molybdate and tungstate. The crude product was finely powdered and shaken up in carbon tetrachloride between the poles of a magnet. The non-magnetic phases settled to the bottom. The compounds  $\text{Ba}_3\text{Cr}_2\text{MoO}_9$  and  $\text{Ba}_3\text{Cr}_2\text{WO}_9$  were found to be quite resistant to attack by dilute hydrochloric acid. It was possible, therefore, to remove the barium molybdate or tungstate impurity from these products by treatment with dilute acid.

X-Ray diffractometer tracings were made of all the products using a General Electric XRD-5 diffractometer. The lattice constants derived from these are given in Table I. The iron and manganese compounds gave patterns corresponding to the cubic ordered perovskite structure. The barium compounds containing chromium all had the hexagonal barium titanate structure. The presence of  $\text{MoO}_2$  and  $\text{BaMoO}_4$  was detected by X-rays in the products prepared by the reaction indicated by eq. 1. Purer

products were formed using the reactants in the proportion shown in eq. 3. The strontium compound  $\text{Sr}_2\text{CrMoO}_6$  did not show any superlattice lines in its diffraction pattern. Prolonged annealing at temperatures from 800 to 1100° failed to produce any evidence of ordering in the structure.

The analysis of the barium iron molybdenum oxide gave barium (as sulfate) 53.21%, molybdenum (as lead molybdate) 18.00%, and iron (by potentiometric titration with Ce(IV)) 11.10%. (Calcd. for  $\text{Ba}_2\text{FeMoO}_6$ : Ba, 53.57; Mo, 18.36; Fe, 10.70.) Analysis of the strontium chromium molybdenum oxide gave molybdenum (as lead molybdate) 24.85% and chromium (iodometric method) 12.01%. (Calcd. for  $\text{Sr}_2\text{CrMoO}_6$ : Mo, 22.89; Cr, 12.41.)

The compounds  $\text{Ba}_2\text{FeMoO}_6$ ,  $\text{Sr}_2\text{FeMoO}_6$ ,  $\text{Ca}_2\text{FeMoO}_6$ ,  $\text{Sr}_2\text{CrMoO}_6$ , and  $\text{Sr}_2\text{CrWO}_6$  were found to be attracted to a magnet at room temperature. The corresponding calcium chromium compounds became magnetic at low temperature. The Curie temperatures are given in Table I. Measurements were made over the temperature range from –180 to 400° for  $\text{Sr}_2\text{CrMoO}_6$  and from –180 to 200° for the others. No magnetic transition was found for the manganese compound above –180°.

## Discussion

The spatial arrangement of the B cations in the idealized ordered perovskite has been described with an accompanying diagram in a previous publication.<sup>4</sup> The achievement of this type of ordering in perovskite compounds having the general formula  $\text{A}_2\text{B}'\text{B}''\text{O}_6$  has been attributed to a large charge difference between the B' and B'' cations.<sup>2,4</sup>

With respect to this, it has been noted that the X-ray pattern for  $\text{Ba}_2\text{FeTaO}_6$  gave no evidence for a superstructure.<sup>7</sup> This would indicate that the iron and tantalum were randomly distributed over the octahedral sites, with the disorder resulting from the small charge difference. The fact that superlattice lines were observed in the diffraction pattern for  $\text{Ba}_2\text{FeMoO}_6$  would suggest that, at the temperature of preparation, the oxidation state of the iron is +2 and that of molybdenum is +6. This then would facilitate the high degree of ordering. The magnetic properties then can be explained by an electron transfer at lower temperatures, whereby both iron and molybdenum would be paramagnetic, allowing superexchange interaction.

This interchange of oxidation states is not possible for the compound  $\text{Ba}_2\text{FeTaO}_6$ , and the absence of superlattice lines for  $\text{Sr}_2\text{CrMoO}_6$  might be attributed to the same type of phenomenon, since it would not be expected that  $\text{Cr}^{+2}$  would exist in an oxygen environment. However,  $\text{Sr}_2\text{CrMoO}_6$  has been shown to have a saturation magnetic moment of 9.20 e.m.u./g., and this indicates partial ordering has occurred. More evidence was brought to bear on this when tungsten was substituted for molybdenum, and the X-ray pattern gave evidence for a superstructure. Theoretical intensities calculated on the basis of a completely ordered structure for  $\text{Sr}_2\text{CrMoO}_6$  show that the ordering reflections should have been observed (Table II). Intensity calculations also were made for some reflections of the  $\text{Sr}_2\text{CrWO}_6$  pattern and, on a relative basis, indicated approximately 50% ordering of the chromium and tungsten. This value also should correspond to that for  $\text{Sr}_2\text{CrMoO}_6$ , since the absence of superlattice

TABLE I  
LATTICE CONSTANTS OF COMPOUNDS  $\text{A}_2\text{B}'\text{B}''\text{O}_6$ <sup>a</sup>

| Compounds                            |                    | a    | b    | c     | Curie temp., °C. |
|--------------------------------------|--------------------|------|------|-------|------------------|
| $\text{Ba}_2\text{FeMoO}_6$          | Cubic              | 8.08 |      |       | 64               |
| $\text{Sr}_2\text{FeMoO}_6$          | Cubic              | 7.89 |      |       | 146              |
| $\text{Ca}_2\text{FeMoO}_6$          | Orthorhombic       | 5.53 | 7.73 | 5.42  | 104              |
| $\text{Ba}_2\text{FeMoO}_{5.5}$      | Cubic              | 8.08 |      |       |                  |
| $\text{Ba}_3\text{Cr}_2\text{MoO}_9$ | Hexagonal          | 5.72 |      | 14.02 |                  |
| $\text{Sr}_2\text{CrMoO}_6$          | Cubic <sup>b</sup> | 7.82 |      |       | 200              |
| $\text{Ca}_2\text{CrMoO}_6$          | Orthorhombic       | 5.49 | 7.70 | 5.36  | –125             |
| $\text{Ba}_3\text{Cr}_2\text{WO}_9$  | Hexagonal          | 5.75 |      | 14.35 |                  |
| $\text{Sr}_2\text{CrWO}_6$           | Cubic              | 7.82 |      |       | 180              |
| $\text{Ca}_2\text{CrWO}_6$           | Orthorhombic       | 5.47 | 7.70 | 5.35  | –130             |
| $\text{Sr}_2\text{MnMoO}_6$          | Cubic              | 7.98 |      |       | °                |

<sup>a</sup> Cell edges in Å. <sup>b</sup> Unit cell is doubled although no superlattice lines were observed. <sup>c</sup> No transition down to liquid nitrogen.

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR  $\text{Sr}_2\text{CrMoO}_6$  INDEXED ON THE BASIS OF THE ORDERED PEROVSKITE STRUCTURE ( $a = 7.82 \text{ \AA}$ .) AND A COMPARISON OF OBSERVED AND CALCULATED

| INTENSITIES      |                   |                  |
|------------------|-------------------|------------------|
| <i>hkl</i>       | <i>I</i> (calcd.) | <i>I</i> (obsd.) |
| 111 <sup>a</sup> | 4.56 (24.59)      | ... (12.46)      |
| 200              | 1.86              | ...              |
| 220 <sup>a</sup> | 100 (100)         | 100 (100)        |
| 311              | 3.20              | ...              |
| 222              | 6.69              | 8.62             |
| 400 <sup>a</sup> | 36.03 (31.26)     | 44.41 (38.67)    |
| 331              | 1.50 (15.61)      | ... (8.55)       |
| 426              | 0.008             | ...              |
| 422              | 37.96             | 40.67            |
| 511              | 1.20              | ...              |
| 440              | 19.70             | 21.02            |
| 531              | 1.35              | ...              |
| 620              | 15.8              | 15.4             |
| 533              | 0.51              | ...              |
| 622              | 1.52              | ...              |
| 444              | 6.60              | 5.73             |
| 711, 551         | 0.83              | ...              |
| 642              | 20.84             | 17.41            |
| 553              | 1.10              | ...              |
| 800              | 3.84              | 3.78             |
| 733              | 0.36              | ...              |
| 822, 660         | 14.74             | 10.74            |
| 751, 555         | 0.88              | ...              |
| 662              | 0.94              | ...              |
| 840              | 16.30             | 12.16            |
| 664              | 12.80             | 9.68             |
| 931              | 1.10              | ...              |
| 844              | 28.30             | 23.61            |
| 933, 771, 755    | 2.88              | ...              |

<sup>a</sup> The intensities in parentheses are for  $\text{Sr}_2\text{CrWO}_6$ .

lines is only a consequence of the smaller scattering factor for molybdenum compared with tungsten.

The relatively high intensities of the 111 and the 311 reflections in the diffraction pattern of the compound  $\text{Sr}_2\text{MnMoO}_6$  suggest that it is highly ordered. It thus would seem reasonable to suppose that the manganese is +2 and the molybdenum is +6 in this compound and that they had remained so at the temperature of formation. No ferrimagnetic properties were observed for this compound down to liquid nitrogen temperatures. The sintered material has a very high electrical resistance. These properties are not in conflict with our conclusions about the oxidation states.

It is of some interest to note that the barium chro-

mium molybdenum oxide adopted the hexagonal barium titanate structure. The purest product was obtained from a mixture corresponding to the composition  $\text{Ba}_3\text{Cr}_2\text{MoO}_9$ , which would seem to support the interpretation of these phases given by Dickinson.<sup>9</sup> Chromium appears to have an especially strong tendency to form metal-metal bonds, for all of the compounds of this type containing barium and chromium have the hexagonal barium titanate structure.

By analogy with the magnetic properties of the rhenium compounds,  $\text{A}_2\text{FeReO}_6$ , an increase in Curie temperature with decreasing A cation size might have been anticipated.<sup>4</sup> The smaller A cation permits more favorable B'-O-B'' superexchange interaction. However, the  $\text{A}_2\text{CrMoO}_6$  and  $\text{A}_2\text{CrWO}_6$  compounds show considerably smaller Curie temperatures for  $\text{Ca}^{+2}$  compared to  $\text{Sr}^{+2}$  in the A position (Table I). For these compounds the smaller calcium ion has favored orthorhombic distortion; this changes the O-B-O angle from the  $180^\circ$  which is most favorable for the magnetic interaction.<sup>5</sup> Thus the magnetic evidence would seem to indicate that in these substances the change of crystal angles due to a smaller A cation is more important to the magnetic interactions than a smaller B-O distance. That the effects of angle and distance on the magnetic interactions are energetically similar is evidenced by the  $\text{A}_2\text{FeMoO}_6$  substances; the strontium compound has a higher Curie temperature than that of the barium compound as predicted on the basis of size, but the smaller calcium ion leads to orthorhombic distortion and an intermediate value for the magnetic transition temperature. On this basis one might conclude that the orthorhombic distortion angle is somewhat larger for  $\text{Ca}_2\text{FeMoO}_6$  than for  $\text{Ca}_2\text{FeReO}_6$ ; the X-ray data do not permit this to be decided. It is obvious that further and more complete examinations of the magnetic properties of these series of compounds are required.

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